Contaminants of Emerging Concern: A Summary of Findings from Monitoring of Major Tributaries Draining to Lake Michigan

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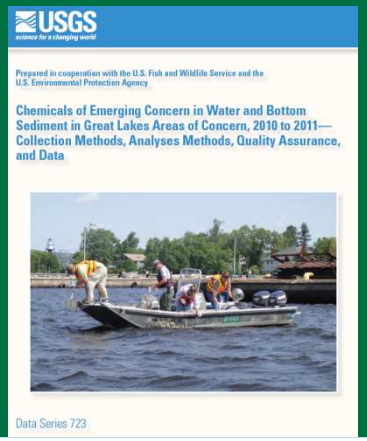
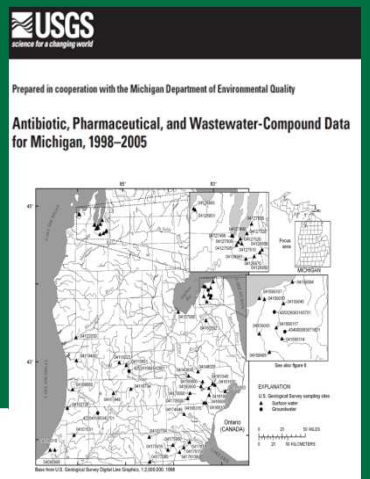
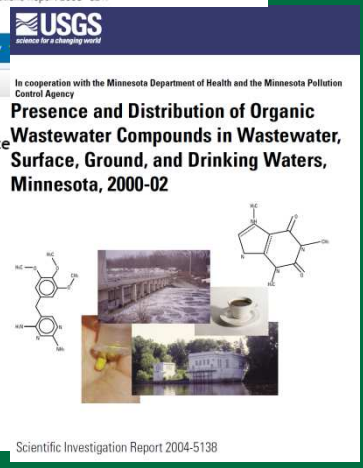
U.S. Department of the Interior
U.S. Geological Survey

Background

- USGS Toxics Substances Hydrology Emerging Contaminants Program (1999-2000) Reconnaissance
- Spurred interest in understanding how CECs impact
- Federal, state, university research has followed
- No systematic study to evaluate the Great Lakes as a whole
  - Great Lakes Restoration Initiative







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Study Design and Sampling

- GLRI baseline conditions and geographic sources of CECs
- 2010-2013, 709 environmental samples
  - 45 field blanks, 52 replicate samples
- Integrated (Equal Width Increment) sampling
  - Some auto-sampling at points
- Bi-annually to monthly depending on location
  - Coverage of 59 sites
  - Variable frequency
- Baseflow and event flows

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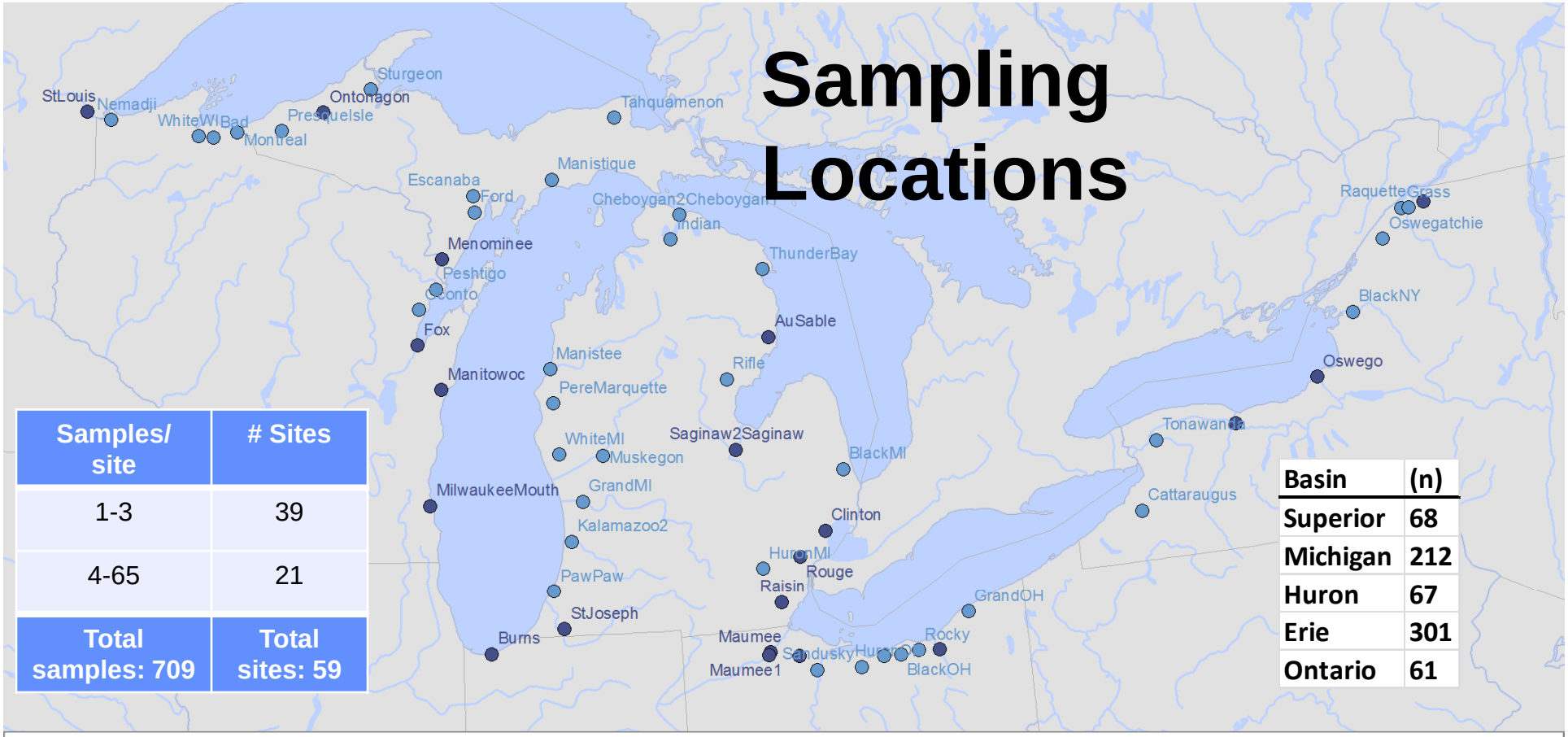
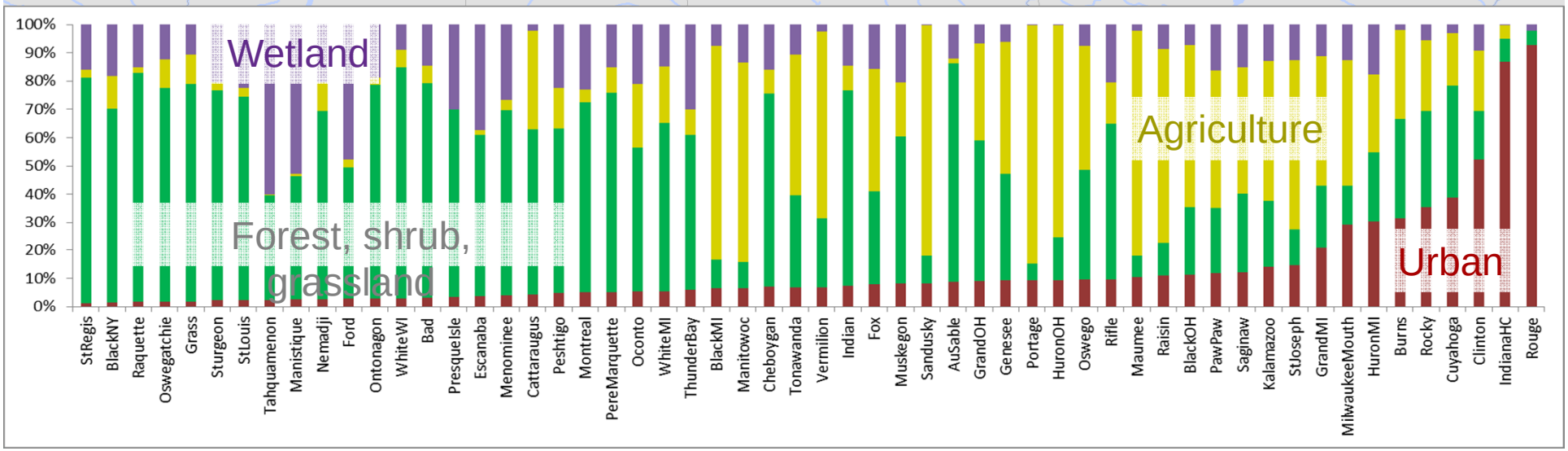
Sampling Locations



Samples/ site	# Sites
1-3	39
4-65	21
Total samples: 709	**Total sites: 59**

Basin	(n)
Superior	**68**
Michigan	**212**
Huron	**67**
Erie	**301**
Ontario	**61**



CEC classes for water samples

- 65 total compounds
- Antimicrobials
- Antioxidants
- Detergent Metabolites
- Dye/Pigment
- Fire Retardant
- Flavor/Fragrance
- Fuel
- Herbicide
- Human Drugs (non-prescription)
- Insecticide
- Other
- PAH
- Plasticizers
- Solvents
- Sterols

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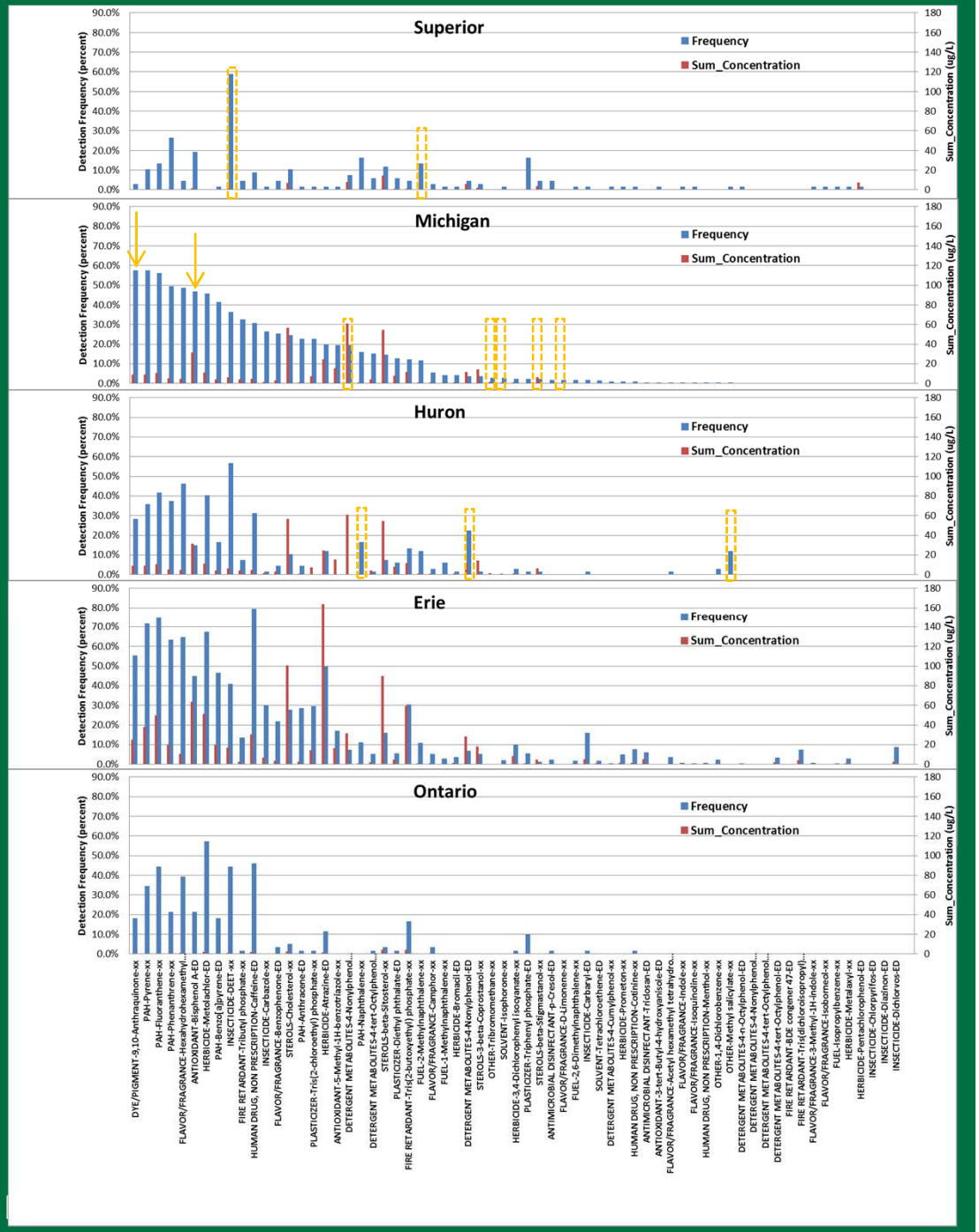
How do Lake Michigan Tributaries Compare to the other Great Lakes Tributaries?

- Most frequent detections of:
  - 9,10-Anthraquinone
  - Bisphenol-A (ED)
- Highest concentrations of:
  - 4-Nonylphenol diethoxylate (ED)
  - beta-Stigmastanol
    - (phytoestrogen)
  - Tribromomethane
    - (multiple uses)
  - Isophorone (solvent)
  - D-Limonene
- Superior Tributaries
  - Most frequent detection of DEET & 2-methylnaphthalene
- Huron Tributaries
  - Most frequent detection of naphthalene, methyl salicylate (mint) & 4-nonylphenol (ED)
- Erie Tributaries
  - Most frequent detections of 27 compounds, highest sum concentration of 39 compounds
- Ontario Tributaries
  - No most frequently detected or highest sum concentration compounds



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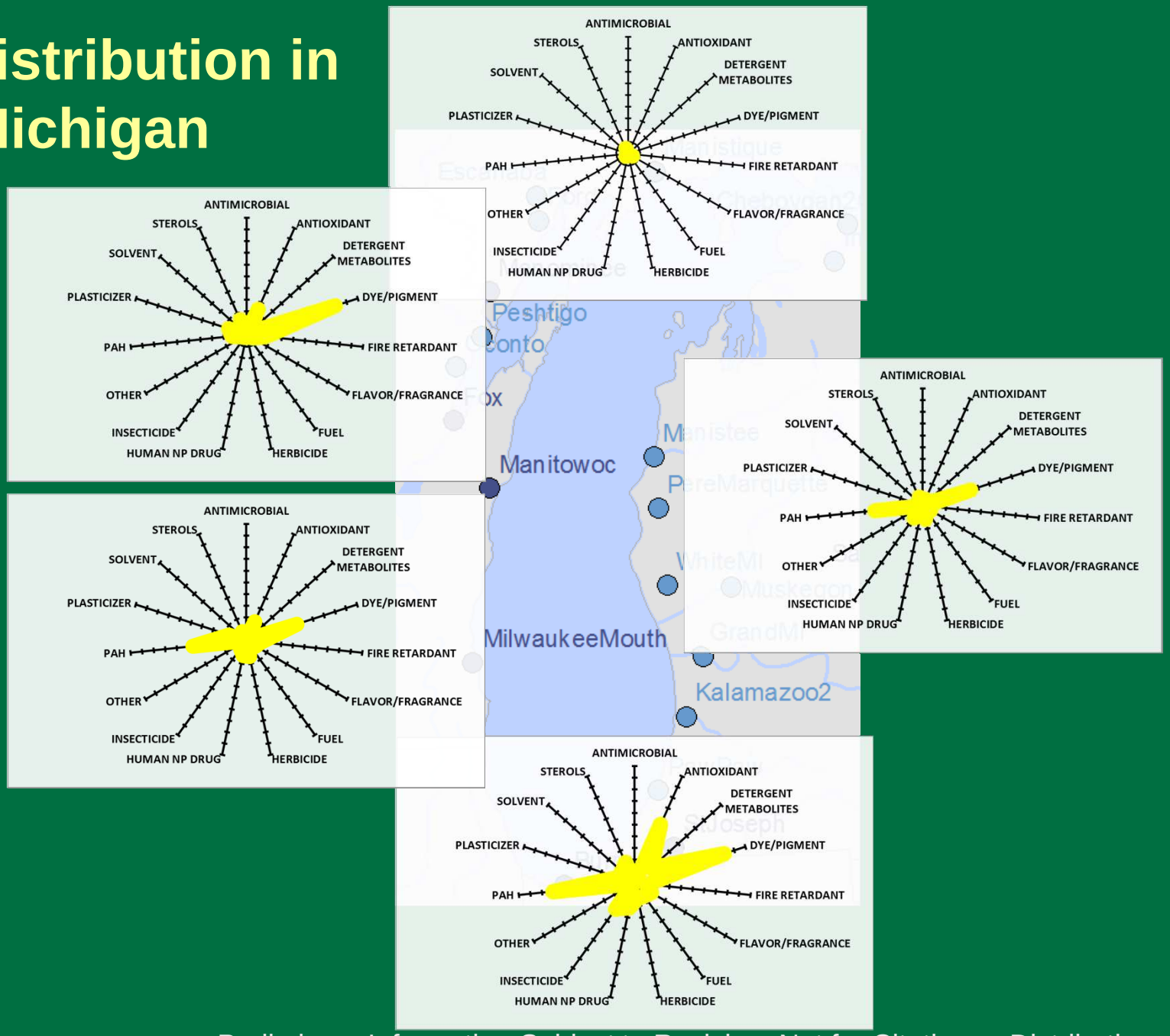
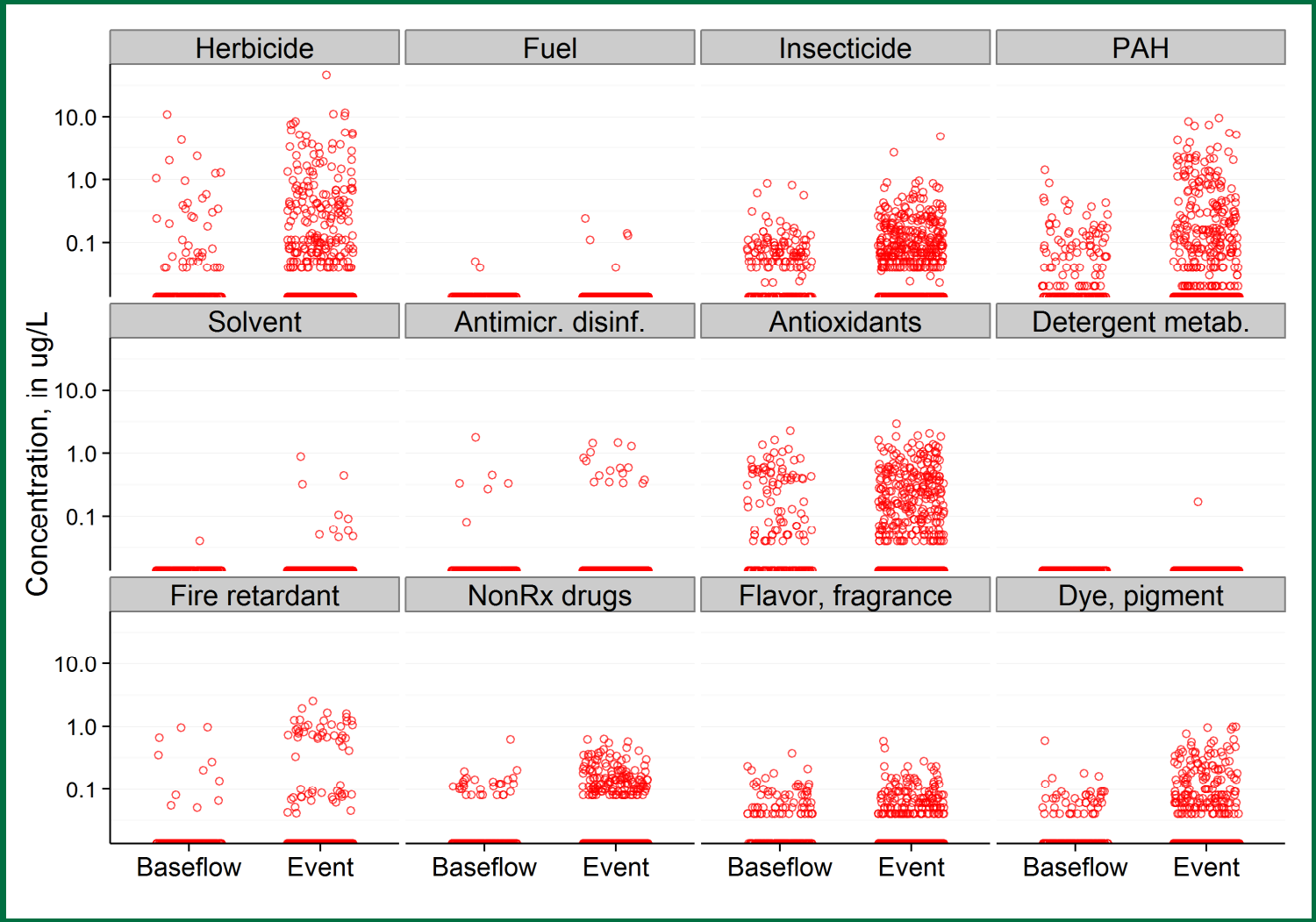
Preliminary

CEC Distribution in Lake Michigan



Preliminary Information-Subject to Revision. Not for Citation or Distribution

CEC Concentration vs Flow Condition



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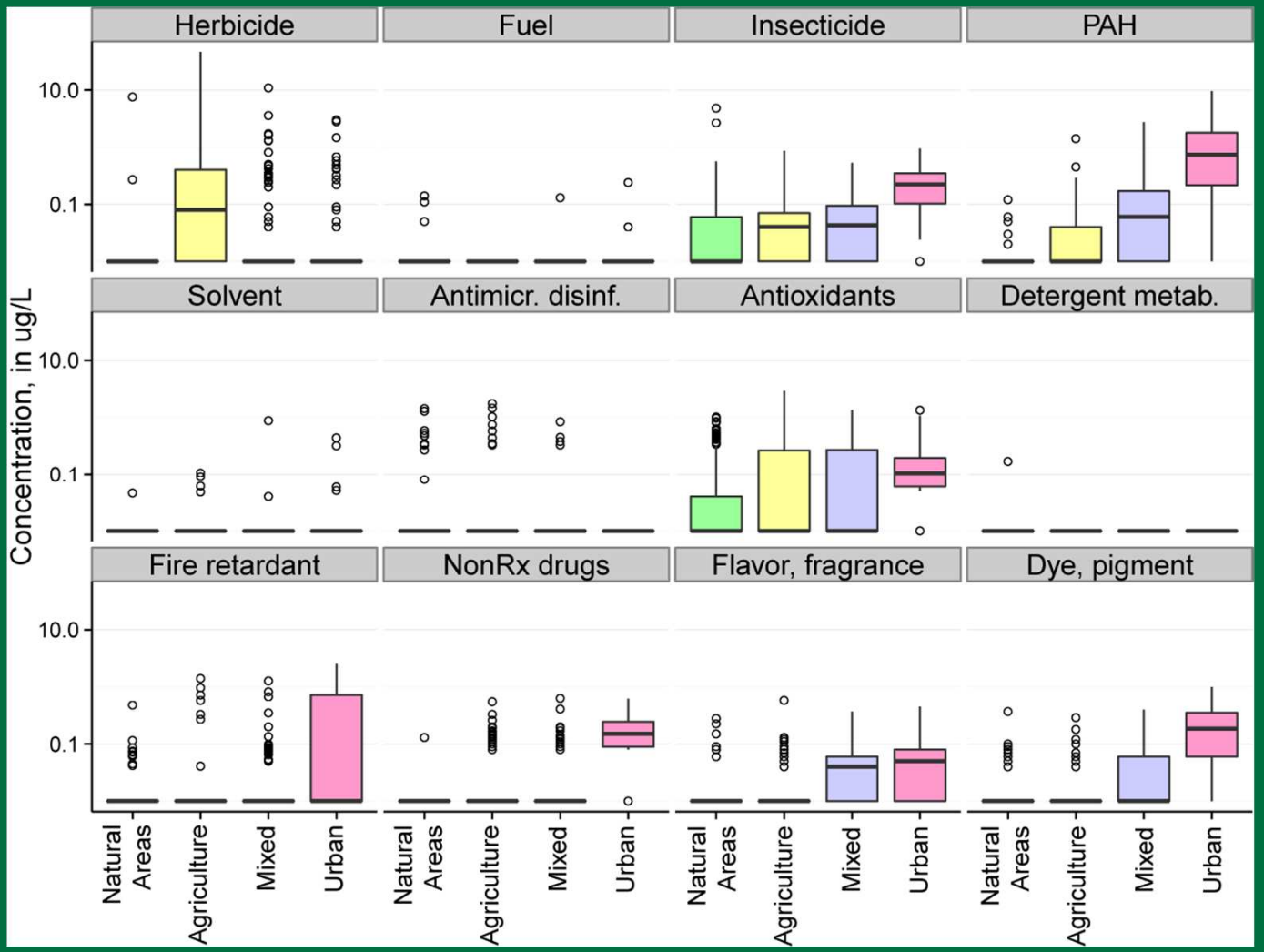
CEC Concentration vs Land Cover



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A different sampling approach?

- **Passive Sampling**
  - Semipermeable membrane device (SPMD)
    - Neutral organic chemicals (high (>3) K_{ow} (PCB, PDBE, dioxins, furans)
  - Polar Organic Chemical Integrative Sampler (POCIS)
    - More water soluble chemicals (low (<3) K_{ow} (pharmaceuticals, illicit drugs, polar pesticides, phosphate flame retardant)
  - Long deployment
  - Integrates to provide an average concentration per unit of time

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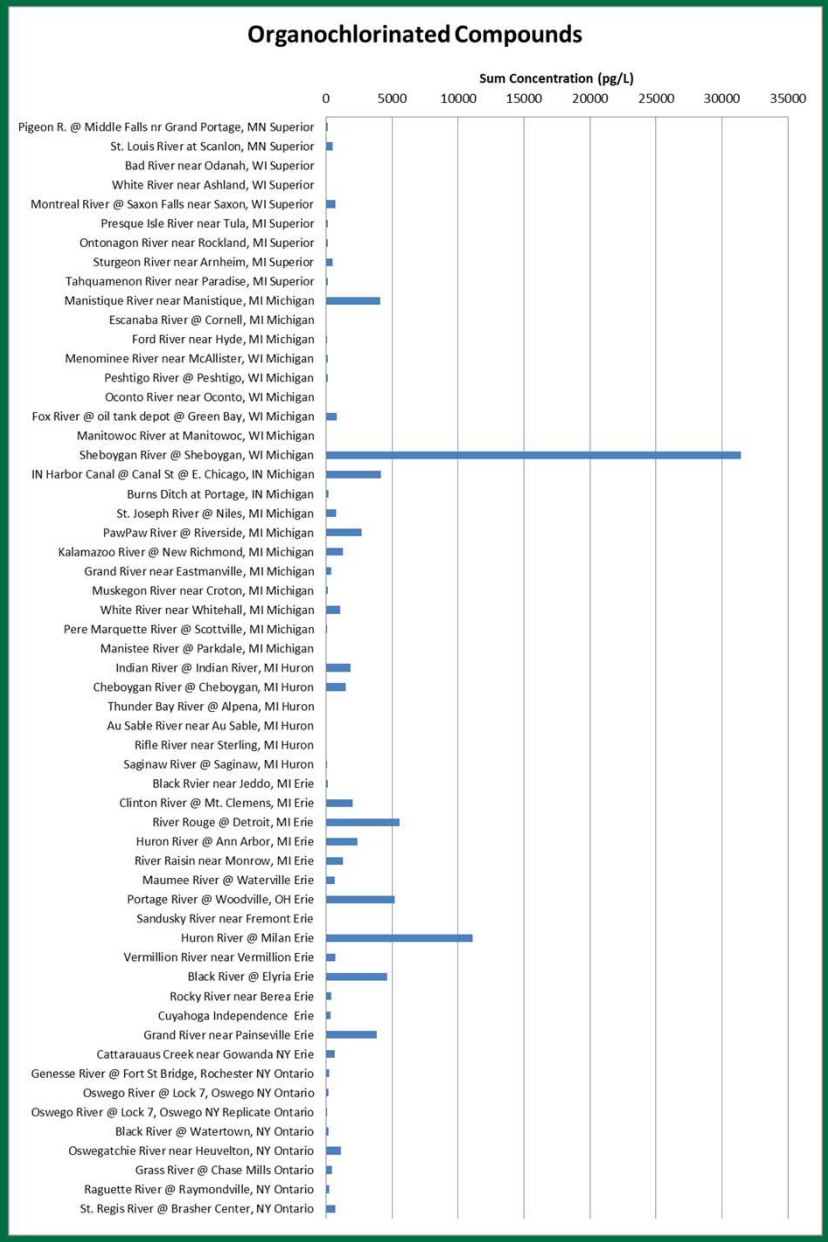
Organochlorinated Compounds

- Trifluralin
- Hexachlorobenzene (HCB)
- Pentachloroanisole (PCA)
- Tefluthrin
- alpha-Benzenehexachloride (α-BHC)
- Lindane
- beta-Benzenehexachloride (β-BHC)
- Heptachlor
- delta-Benzenehexachloride (δ-BHC)
- Dacthal
- Chlorpyrifos
- Oxychlordane
- Heptachlor Epoxide
- trans-Chlordane
- trans-Nonachlor
- o,p'-DDE
- cis-Chlordane
- Endosulfan
- p,p'-DDE
- Dieldrin
- o,p'-DDD
- Endrin
- cis-Nonachlor
- o,p'-DDT
- p,p'-DDD
- Endosulfan-II
- p,p'-DDT
- Endosulfan Sulfate
- p,p'-Methoxychlor
- Mirex
- cis-Permethrin
- trans-Permethrin



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Total PCB

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PBDEs

- PBDE-28
- PBDE-47
- PBDE-99
- PBDE-100
- PBDE-153

- Grand River
  - Mostly PBDE 153 & 147
  - 10x time higher than any other monitored tributary in the Great Lakes
  - Follow up study being conducted

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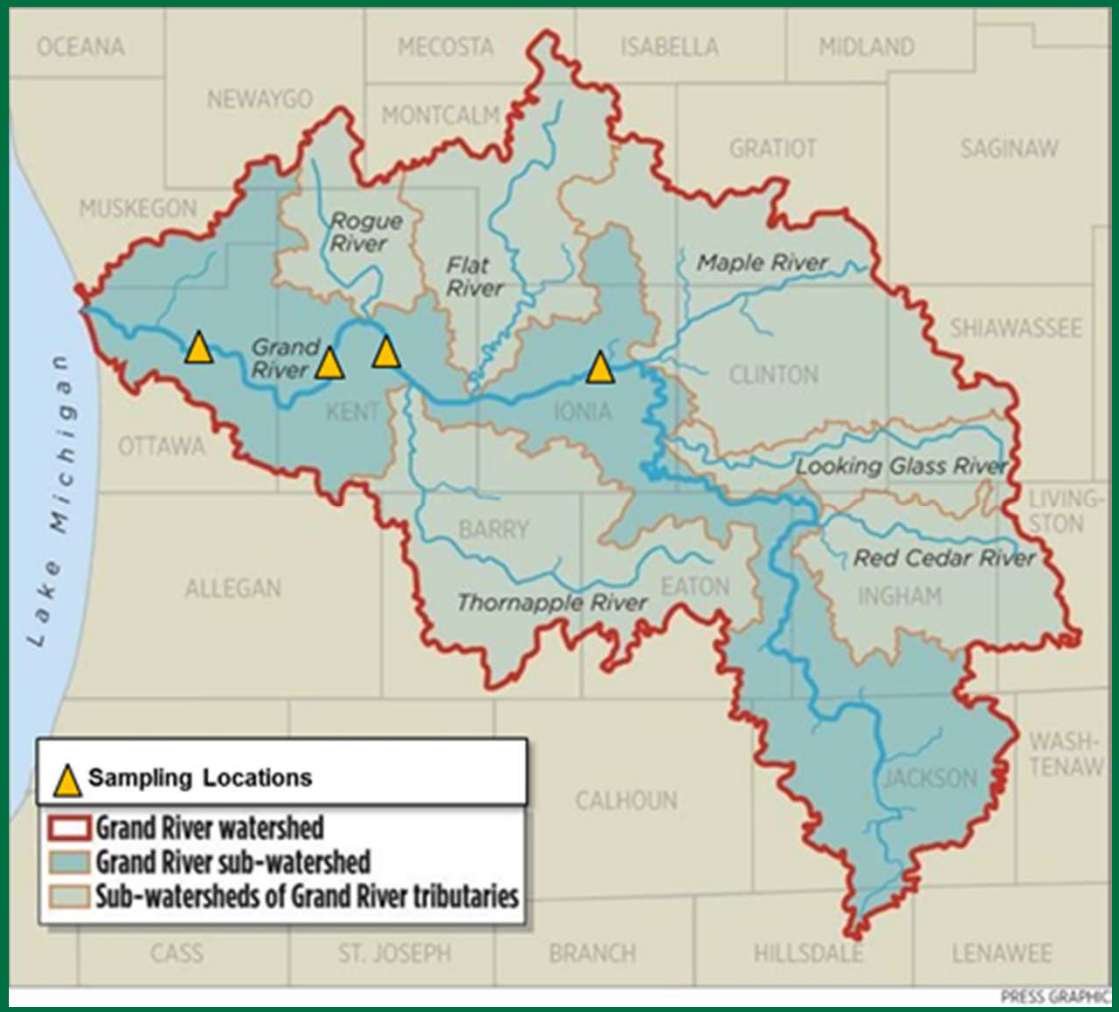
PBDE Follow up

- Grand River at Eastmanville, MI was the site where the original elevated PBDE concentrations were detected
- Followed up, with more dispersed spatial sampling to isolate the lower Grand River
  - Grand River
    - at Ionia, MI
    - at Ada, MI
    - at Grand Rapids, MI
    - at Eastmanville, MI
  - Thornapple river is a hypothesized source
- More sampling?
- Potential for bioaccumulation
  - But currently only a 1-month time/flow composited sample



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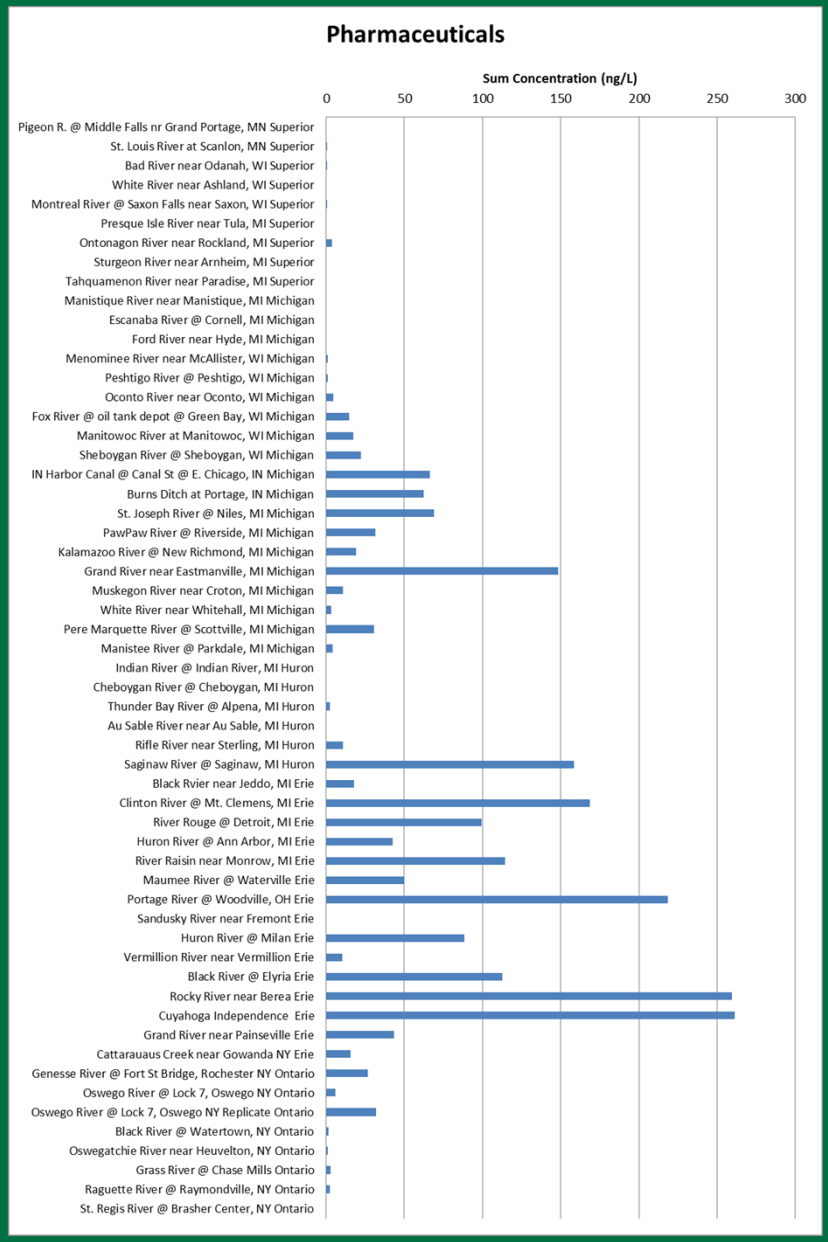
Pharmaceuticals

Cotinine
Acetaminophen
Albuterol
Cimetidine
1,7-dimethylxanthine
Ranitidine
Codeine
Caffeine
Trimethoprim
Thiabendazole
Sulfamethoxazole
Azithromycin
Carbamazapine
Diltiazem
Dehydronifedipine
Erythromycin
Warfarin
Fluoxetine
Miconazole
Diphenhydramine

Fluoxetine
Norfluoxetine
Bupropion
Venlafaxine
Citalopram
Paroxetine
Fluvoxamine
Duloxetine
Norsertraline
Sertraline
Carbamazepine

Aspirin
Clofibric Acid
Diclofenac
Enaliprilat
Furosemide
Gemfibrozil
Hydrochlorothiazide (HCTZ)
Ibuprofen
Ketoprofen
Naproxen
Simvastatin
Triclocarban
Triclosan



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Conclusions

Lake Michigan had the most frequent detections of BPA, and highest observed concentrations of 4-Nonylphenol diethoxylate, tributaries ranked 2nd largest array of detected CECs

There were geographic differences in the array, frequency, and additive concentrations of CECs around Lake Michigan

Mean concentrations of CECs were typically higher during event flow when compared to baseflow

Industrial and household chemicals (dyes, fragrances, PAHs, flavors, flame retardants) were typically elevated in sites with dominant urban land cover

Use of passive sampling techniques allowed for the identification of priority sampling locations for future studies, and detected compounds not detected using traditional water-sampling techniques. Could provide a geographic guide for biota sampling

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Future Directions

- Evaluate occurrence of CECs in 2011-2013 study with respect to fecally-derived bacterial pathogens
- Using a “contaminant class of the year” approach, evaluate different groups of CECs at major Great Lakes tributaries
  - EFFECTS!
    - YES
    - Metabolomics, transcriptomics, USEPA Toxicity ForeCaster (ToxCast™)
    - USEPA, USACE, USFWS, USGS

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